



On the kinetics and mechanisms of photolytic/TiO₂-photocatalytic degradation of substituted pyridines in aqueous solutions

David R. Stapleton^a, Ioannis K. Konstantinou^b, Dionissios Mantzavinos^c,
Dimitra Hela^d, Maria Papadaki^{a,b,*}

^a Chemical Engineering, IPSE, School of Process Environmental and Materials Engineering, University of Leeds, Leeds LS2 9JT, UK

^b Department of Environmental and Natural Resources Management, University of Ioannina, Seferi 2, GR-30100 Agrinio, Greece

^c Department of Environmental Engineering, Technical University of Crete, Polytechnioupolis, GR-73100 Chania, Greece

^d School of Natural Resources and Enterprises Management, University of Ioannina, Seferi 2, GR-30100 Agrinio, Greece

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ABSTRACT

Pyridine and pyridine derivatives are extensively used for the production of pesticides, medicinal drugs, industrial solvents, dyes, rubber chemicals etc. They are encountered in their wastewaters and due to their hazardous effects on ecosystems and human health, their removal is imperative. However, the methods for their treatment need to be improved or replaced by more effective alternatives. With this in mind and following our previous work on photolytic treatment of 2-halogenated pyridines (2-HalPys), the combined photolytic/photocatalytic (TiO₂ P-25) at 254 nm degradation and mineralisation of 2-chloropyridine (2-CPY), 2-fluoropyridine (2-FPY) and 2-hydroxypyridine (2-HPY), a major photolytic product of all 2-HalPys but 2-FPY are studied in a range of conditions. In order to probe into the mechanisms and factors affecting their degradation, the effects of pH, radical scavenger *tert*-butanol and inorganic ions, were examined. The former had a substantial impact on 2-CPY photocatalytic removal rate, which, however, remained practically unaffected by the latter. 2-CPY photocatalytic removal was faster at near neutral pH. 2-HPY degradation was faster in the presence of TiO₂, low pH and in the presence of F[−] or SO₄^{2−} anions. On the contrary, Cl[−] anions or the presence of *tert*-butanol had a pronouncedly detrimental effect on 2-HPY degradation rate. Main reaction by-products accompanying the purely photocatalytic destruction of 2-CPY and 2-FPY were identified. Complete total organic carbon removal was achieved in all cases.

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1. Introduction

Aromatic N-heterocycles like pyridine and pyridine derivatives (PDs) have received a great attention because of their occurrence in the environment and their hazardous effects on ecosystems and human health [1,2]. Numerous man-made compounds such as pesticides, medicinal drugs, industrial solvents, dyes, rubber chemicals etc. are based on PD precursor compounds including, insecticides such as chloropyrifos and acetamiprid, herbicides such as clopyralid, picloram, diflufenican and triclopyr, biocides such as zinc pyrithione antihistaminic, antirhythmic and antibiotic pharmaceuticals such as pheniramine, disopyramide and enoxalin, respectively. PDs may enter the environment as a consequence of the widespread use of such pesticides as well as from urban and

industrial effluent discharges [1,3,4]. Halogenated PDs are persistent compounds, for the degradation of which, photochemical advanced oxidation processes (PAOPs) appear promising. In particular, TiO₂ based heterogeneous photocatalysis has been extensively used to effectively degrade many organic pollutants such as dyes, pesticides, surfactants, etc. including PDs and offers an advanced technology for wastewater treatment [1,5–8].

The present research focuses on the mechanisms of the photocatalytic degradation of selected pyridines with potential future applications on wastewater treatment in mind and its objectives are closely linked with the findings of our previous photolytic studies on 2-chloropyridine (2-CPY), 2-bromopyridine (2-BPY), 2-iodopyridine (2-IPY), 2-fluoropyridine (2-FPY) and 2-hydroxypyridine (2-HPY), shown in detail elsewhere [9–12]. 2-Halogenated pyridine (2HalPy) photolytic degradation and potential mechanisms of their destruction are shown in our previous work [9]. 2-CPY, 2-BPY and 2-IPY are readily removed photolytically, upon irradiation with UV light at 254 nm producing 2-HPY as an early stage, major intermediate compound. Their photolytic mineralisation however, was found to be slow, probably because 2-HPY is

* Corresponding author at: Department of Environmental and Natural Resources Management, University of Ioannina, Seferi 2, GR-30100 Agrinio, Greece.
Tel.: +30 2641074184; fax: +30 2641074176.

E-mail addresses: mpapadak@cc.uoi.gr, m.papadaki@leeds.ac.uk (M. Papadaki).

highly resistant to photolysis. On the other hand, the photolytically treated 2-FPY, which does not produce 2-HPY, was mineralised faster than the other 2-halogenated pyridines. 2-HalPyS rapidly dehalogenated when subjected to direct photolysis. Their dehalogenation resulted in a sharp drop of solution pH which, however, did not affect the photolytic removal rate of the substrate. On the contrary, 2-HPY photolytic destruction and removal was found to advance faster at low pH but was unaffected by the kind of halogen acid [10]. Preliminary photocatalytic measurements at 254 nm employing 2-CPY and different quantities of suspended photocatalyst [11,12], showed that mineralisation of those compounds is faster in the presence of the photocatalyst. However, the photolytic removal of 2-CPY at 254 nm can have a small but measurable contribution even in the presence of photocatalyst.

The present study was thus performed in order to probe into the mechanisms of representative 2-HalPy photo-degradation and acquire the data and knowledge which will allow to examine whether a combination of photolytic and/or photocatalytic processes can form an efficient method of treatment of wastewaters containing compounds of this family. More specifically, it was viewed that the photolytic treatment of 2-CPY, 2-BPY, 2-IPY, which results in fast 2-HalPy dehalogenation and predominantly produces 2-HPY could potentially be employed for 2-HalPy dehalogenation; this step could be then followed by a common photocatalytic treatment step. However, in order to decide on the most effective use of a combination of PAOPs to achieve mineralisation of specific pollutants, the in-depth knowledge of the chemistry of their degradation pathways is the only means to avoid empirical approaches and to design environmentally safer, sound and more economical processes.

Towards that long term objective, 2-CPY, 2-FPY and 2-HPY photocatalytic (TiO_2 P-25) removal and mineralisation under different conditions was studied here and degradation products have been identified. The selected compounds were: 2-CPY as a representative compound forming 2-HPY when treated photolytically, 2-FPY because during photolytic treatment it does not practically form 2-HPY and finally, 2-HPY in order to assess the effect of TiO_2 photocatalyst on the degradation of this resistant to photolytic treatment key intermediate compound. Measurements were performed in the presence of TiO_2 P-25 at 254 nm (where photolysis of 2-HalPy only marginally contributes) and at wavelengths above 290 nm, where the original substrate does not practically absorb [13,14] and, consequently, its photolysis can be totally neglected.

2. Experimental and analytical

2.1. Materials

2-Chloropyridine ($\text{C}_5\text{H}_4\text{NCl}$) and 2-fluoropyridine ($\text{C}_5\text{H}_4\text{NF}$) of purity greater than 98% were supplied by Fluka. 2-Hydroxypyridine ($\text{C}_5\text{H}_4\text{NOH}$) of 97% purity was supplied by Aldrich. Aqueous solutions were made using deionised water, which was prepared by an Elga B114 Deioniser using C114 cartridges. Titanium dioxide (TiO_2 P-25) of purity greater than 97% was supplied by Degussa (21 nm of average particle size, 70:30 anatase:rutile mixture, HCl content less than 0.3 wt.%). *tert*-Butanol ($\text{C}_4\text{H}_{10}\text{O}$) of 99% purity was supplied by Riedel-de Haen. All reagents were used without further treatment or purification.

2.2. Combined photolytic/photocatalytic degradation at 254 nm

The basic experimental set-up employed for illumination at 254 nm is described in detail elsewhere [11]. Experiments at 254 nm were performed with 0.4 L of aqueous solutions at an initial

substrate concentration of 2.7 ± 0.4 mM at a constant temperature of 50°C with air sparging. In all photocatalytic experiments performed at 254 nm, 1 g L^{-1} of TiO_2 was suspended in the solution via vigorous magnetic agitation. The selection of this photocatalyst concentration is justified elsewhere [11,15]. In all cases, the substrate was mixed with the photocatalyst in the dark (to prevent potential 2-CPY photolysis) for 60 min prior to the initiation of UV irradiation to reach substrate adsorption equilibrium on the catalyst. As in the case of 2-CPY photolysis [9], the effects of the addition of radical scavenger *tert*-butanol, pH and that of different ions were assessed. The effects of the latter two factors were studied via the addition of HCl, NaCl, HF and H_2SO_4 . Unless otherwise stated, the molar ratio of 2-HPY:acid/salt, was 1:1. The substrate solution was first mixed with the acid or salt, followed by photocatalyst addition.

Experiments employing *tert*-butanol as a radical scavenger were performed. The initial molar concentration ratio of *tert*-butanol:substrate was approximately 6.5:1. Experiments were conducted either without pH control or with pH control near the solution initial natural value of about 7–8; the latter was kept constant via a manual drop-wise addition of 0.01 M NaOH aqueous solution.

Aliquots were periodically drawn from the reactor, filtered through $0.22\text{ }\mu\text{m}$ membrane filters to remove catalyst particles and analysed by means of high performance liquid chromatography (HPLC, LaChrom Hitachi). Total organic carbon (TOC) was also measured using a Shimadzu 5050 TOC analyser. Details of HPLC and TOC analysis are given elsewhere [9].

In order to examine if the original substrates are purged with air, experiments were performed in the dark under vigorous purging at a flowrate of 400 mL min^{-1} .

2.3. Photocatalytic degradation at wavelengths greater than 290 nm

Purely photocatalytic experiments at wavelengths greater than 290 nm were conducted in a simpler system without temperature control, i.e. in a 200 mL Pyrex UV reactor equipped with a diving Philips HPK 125 W high-pressure mercury lamp. The lamp was jacketed with a water-cooled Pyrex filter restricting the transmission of wavelengths below 290 nm. A tap water cooling circuit was used to keep the temperature constant at $30\text{--}35^\circ\text{C}$. The effects of direct photolysis can be ruled out in this system as the emittance wavelength of the UV lamp is well above the region where the employed pyridines absorb (i.e. $>290\text{ nm}$). 2-CPY and 2-FPY initial concentration was 0.1 g L^{-1} and the photocatalyst concentration was in the range $0.5\text{--}2.5\text{ g L}^{-1}$. Products were analysed using a Shimadzu QP2010 GC–MS, according to the methodology presented in our previous work [9]. In these experiments, the whole reactor volume was used for GC–MS product identification, while other analyses were not performed. Compounds were identified comparing their mass spectra with (i) those found in the NIST library, (ii) those reported in the literature, (iii) by interpretation of mass spectra (IOS), and (iv) original standards (where possible).

3. Results and discussion

3.1. Combined photolytic/photocatalytic degradation of 2-CPY at 254 nm

Kinetic data have been collected for the combined photolytic/photocatalytic treatment of aqueous solutions of 2-CPY at 254 nm, at different conditions. Representative results are shown in Fig. 1. Fig. 1a shows concentration profiles as a function of time, while Fig. 1b shows typical pH profiles for measurements at controlled and solution natural pH. As already discussed by Stapleton et al. [11], the photolytic degradation of the substrate at 254 nm also

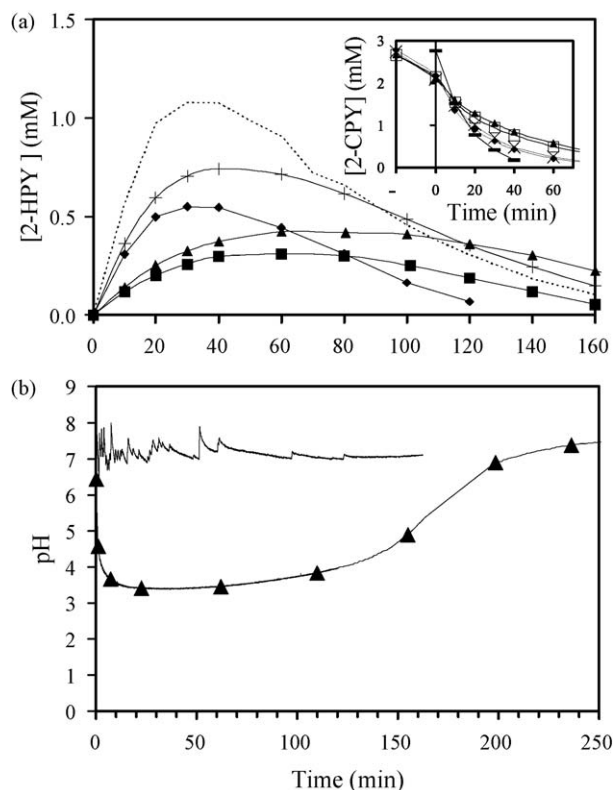


Fig. 1. Photolytic and photocatalytic (1 g L^{-1} P-25) 2-CPY and 2-HPY degradation profiles as a function of time at 50°C under natural and controlled pH with and without *tert*-butanol. (a) Main figure. [2-HPY]: (---) photolytic; (+) controlled pH and radical scavenger; (\diamond) controlled pH; (\blacktriangle) natural pH and radical scavenger; (\blacksquare) natural pH. Embedded figure. [2-CPY]: (---) photolytic; (X) controlled pH and radical scavenger; (\diamond) controlled pH; (\blacktriangle) natural pH and radical scavenger; (\square) natural pH. (b) Typical profile of pH change during 2-CPY photocatalytic degradation with (---) controlled pH; (\blacktriangle) natural pH.

contributes; however, in the presence of 1 g L^{-1} of photocatalyst its overall contribution is substantially reduced.

Although the photolytic 2-CPY removal rate was found to be unaffected by pH [9], its photocatalytic degradation rate was found to depend on pH. This is attributed to the substrate adsorption, which typically depends on pH [16,17]. As can be seen in the inset Fig. 1a, 2-CPY photocatalytic removal is faster at higher (controlled) pH values. Adsorption of 2-chloropyridine on TiO_2 takes place through the formation of hydrogen bonding and interaction with electron transfer at Lewis acidic surface sites as reported by Dines et al. [18]. In a similar study with pyridine, Zhao et al. [19] found that the lowest reaction rate of pyridine appeared at about pH 5. This was because at acidic pH, TiO_2 surface was positively charged while pyridine ($\text{pK}_a = 5.23$) was also protonated and stabilized, resulting in repulsion from TiO_2 surface. In the present research protonation of 2-chloropyridine ($\text{pK}_a = 0.72$) is unlikely to occur; thus, because of the amphoteric nature of TiO_2 surface, H-bonded and Lewis acid site-coordinated 2-CPY molecules on TiO_2 can justify 2-CPY increased adsorption at pH 6.5–8. Additionally, at $\text{pH} > 6$, negative charges enhance the transportation of holes to TiO_2 surface, which react with OH^- and H_2O and generate $\bullet\text{OH}$ radicals [19].

2-CPY photocatalytic removal rate was marginally affected by the presence of *tert*-butanol. As can be seen in Fig. 1 (inset Fig. 1a), the presence of a very high concentration of this radical scavenger resulted in an insignificant reduction of 2-CPY photocatalytic removal rate, thus suggesting that the reaction rate is scarcely affected by the presence of hydroxyl radicals. Smaller concentrations of this radical scavenger have also been tested but they had no measurable effect on 2-CPY photocatalytic removal rate (data

not shown). Therefore, 2-CPY photocatalytic destruction should proceed largely by charge transfer when 2-CPY is adsorbed on the TiO_2 surface and to a very limited extent by hydroxyl radical attack in the bulk of the liquid [20,21]. This, further supports that higher 2-CPY removal rate under controlled pH should be predominantly due to the greater substrate adsorption on the photocatalyst.

2-HPY is the first major 2-CPY photolytic product, which can be further destroyed upon prolonged irradiation. Consequently, its concentration in the reaction solution at any time depends on both its production and decomposition rates. The effects of photocatalyst presence, pH and radical scavenger on 2-HPY concentration profile can be seen in Fig. 1a (main figure). 2-HPY concentration in combined photolysis/photocatalysis under any conditions is lower than its concentration during 2-CPY photolytic treatment under the same conditions. Thus, the presence of photocatalyst has resulted in a significant reduction of 2-HPY bell-shaped profile. In order to investigate the 2-HPY rate of decomposition alone, experiments at controlled conditions were performed using 2-HPY as the original substrate.

3.2. Combined photolytic/photocatalytic degradation of 2-HPY at 254 nm

The 254 nm photolytic destruction of all 2-HalPys but 2-FPY predominantly results in 2-HPY production. The concentration of TiO_2 employed in 2-HPY experiments (1 g L^{-1}) is relatively high, so that it substantially blocks the light [11], thus, given 2-HPY low absorbance at 254 nm [13,22] photolytic 2-HPY degradation can be considered insignificant.

The normalised concentration history of the substrate under different conditions is shown in Fig. 2a. Concentration values at -60 min were measured before the photocatalyst addition. Time zero corresponds to the initiation of UV irradiation. In the embedded Fig. 2a the adsorption on the photocatalyst is shown. Fig. 2b shows the pH history of the same experiments. There are seven curves shown in each figure, in six of which addition of anions has taken place. Two of those correspond to different amounts of NaCl added (stoichiometric and in excess), the addition of which resulted in an initial solution pH 5.7, just below the natural solution initial pH (6.7); one curve shows the effect of stoichiometric HCl addition (initial pH 2.86), while another shows the addition of H_2SO_4 (initial pH 2.45); finally, there are two curves corresponding to the addition of stoichiometric amount of HF (initial pH 3.3), as well as sufficient HF so as to reach the same initial pH as the one reached by HCl, i.e. 2.86. The pH of the latter measurement was maintained at the same value for the first 200 min and started rising well after complete substrate removal, reaching a final value of 4 which was maintained until complete substrate mineralisation.

As can be seen in Fig. 2a the addition of chloride ions, either from HCl or NaCl (in large amounts) resulted in a decreased rate of degradation (increasing the time for 90% 2-HPY removal from ca. 220 to 330 min), while the addition of NaCl in stoichiometric amounts had little effect on this rate. At the same time, both experiments where NaCl was added had the same pH history for the first 200 min (70% substrate removal), which, for the same length of time, was higher than the pH of the experiment where HCl was added (Fig. 2b).

The addition of HCl had the most notable detrimental effect on 2-HPY destruction rate and could be attributed to synergistic effects of pH reduction and Cl^- addition. On the other hand, the addition of either HF or H_2SO_4 practically doubled 2-HPY destruction rate (reducing the time for 90% 2-HPY removal from ca. 220 to approximately 120 min). The solution pH in the latter measurements was just below 3 until complete substrate removal.

The distinctly different effects that different acids had on 2-HPY removal rate indicate that the lower rates in the presence of HCl or

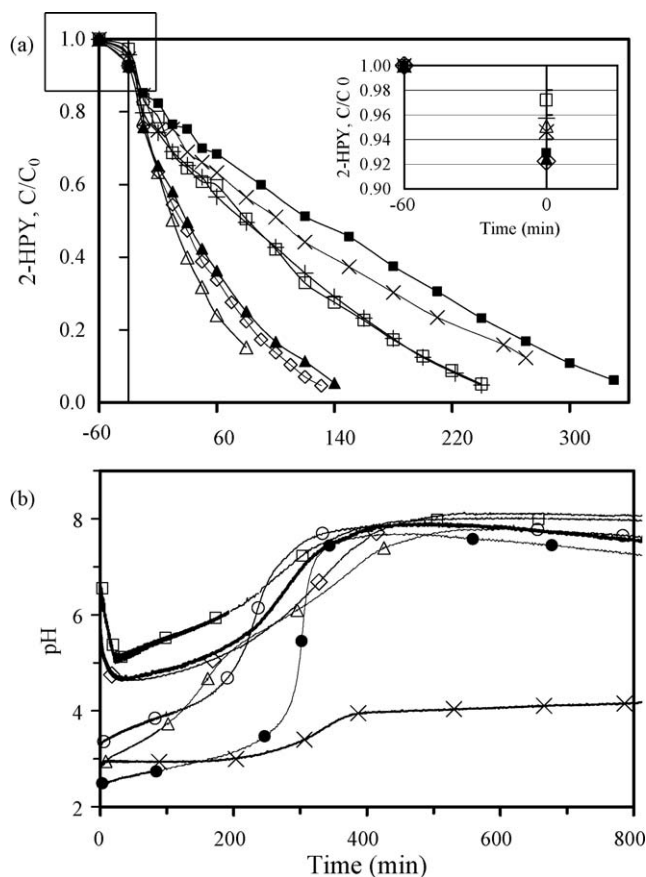


Fig. 2. (a) pH and anion effect on 1 g L^{-1} TiO_2 -photocatalytic degradation of 2-HPY. (■) with HCl; (X) with 2.5:1 NaCl:2-HPY (molar ratio); (+) with NaCl; (□) no addition of salt or acid; (▲) with H_2SO_4 ; (◇) with HF; (△) with HF that results in the same pH as in the experiment with stoichiometric HCl addition. The embedded figure is magnification of the indicated top left corner of the main figure. (b) Change of pH during the above experiments. (△) with HCl; (◇) with 2.5:1 NaCl: 2-HPY (molar ratio); (–) with NaCl; (□) no addition of salt or acid; (●) with H_2SO_4 ; (○) with HF; (X) with HF that results in the same pH as in the experiment with stoichiometric HCl addition.

NaCl cannot be attributed to pH, but to the presence of chloride anions themselves. These ions act as OH^\bullet radical scavengers as well as hole scavengers according to previous findings in the literature. A number of researchers [23–28] found that concentrations of inorganic anions (including Cl^-) up to 0.1 M had limited effect on degradation rate. Liao et al. [23], however, found that in $\text{UV}/\text{H}_2\text{O}_2$ systems the scavenging effect decreases with increasing pH up to pH 6. In the present study only 3.16 mM HCl were sufficient to provoke measurable OH^\bullet radical scavenging at pH 2.86. On the other hand, the scavenging effect caused by the same amount of NaCl at a higher solution pH was less pronounced, which is consistent with the findings of Liao et al. [23]. The mechanism by which this scavenging effect occurs is described by Yu and Barker [25]. It involves three reversible steps where OH^\bullet react with chloride ions to form Cl^\bullet and Cl_2^\bullet .

The addition of HF, on the other hand, doubled the degradation rate. The addition of the stoichiometrically equivalent to 2-HPY HF lowered the pH to 3.3. Further addition of HF to obtain the same pH as the initial pH reached following addition of HCl (2.86), resulted in a further increase of the 2-HPY removal rate. It is well documented that free fluoride ions cannot be oxidized by the valence holes; they adsorb on the surface of TiO_2 and displace surface bound hydroxyl radicals [27,29–31]. Minerio et al. [30] found that photocatalytic degradation of phenol with illuminated TiO_2 proceeds 90% through surface bound hydroxyl groups and 10% through direct interaction with holes. In the same study, they

found that the addition of fluoride ions resulted in elimination of the direct hole interaction, thus resulting in an almost 100% degradation through free hydroxyl radicals. Photocatalytic oxidation reactions taking place on F/TiO_2 systems seem homogeneous-like in their reactive nature because of the production of mobile hydroxyl radicals. Phenol, 4-*tert*-butyl pyridine and some persistent compounds such as cyanuric acid were found to degrade faster in F/TiO_2 systems than under typical TiO_2 conditions [30–32]. These observations further support the hypothesis of hydroxyl radical attack as the predominant reaction pathway of the photocatalytic degradation of 2-HPY.

An equimolar with 2-HPY amount of H_2SO_4 was also added to the 2-HPY/ TiO_2 mixture, yielding a pH of 2.43; 2-HPY subsequent removal rate was almost doubled. The role of SO_4^{2-} ions in the photocatalytic oxidation is under active investigation and the sulfation of TiO_2 was recently acknowledged as a means of enhancing its catalytic and photocatalytic activity [33]. SO_4^{2-} ions could be adsorbed onto the catalyst surface, modifying surface properties such as acidity, area, electron–hole recombination, etc. [33,34]. The improved photocatalytic activity of sulfated TiO_2 towards organic substrates such as benzene and phenol was attributed to the increase of surface area and surface acidity thus, increasing the adsorption of the pollutant [35,36]. The enhanced activity could be also due to a rise of the electron accepting capacity originating from a probable increase in Lewis acid sites and a subsequent decrease in the recombination of holes and electrons [37]. The formation of less reactive $\text{SO}_4^{\bullet-}$ radicals was also proposed by other researchers [38] but according to recent findings it is not relevant with aqueous light-irradiated oxidation processes [39]. The degradation rate achieved with the use of H_2SO_4 is not as high as that observed for HF. This is possibly because of the displacement of surface bound hydroxyl groups by fluoride ions and production of homogeneous-type hydroxyl radicals.

An additional experiment was performed in the presence of 3 g L^{-1} of *tert*-butanol (data not shown) and this almost halved the rate of 2-HPY photocatalytic destruction at 1 g L^{-1} TiO_2 although the same scavenger concentration under identical otherwise conditions had practically no effect on 2-CPY photocatalytic removal rate.

Comparison of 2-HPY removal rates in the presence of different acids and salts, with or without radical scavengers suggest that this reaction is faster at low pH and occurs with hydroxyl radical attack. The presence of Cl^- anion results in hydroxyl radical scavenging effects, which are more pronounced at lower pH.

As can be seen in Fig. 2a (inset), at solution natural pH (ca. 7), the adsorption of 2-HPY ($\text{pK}_{a1} = 0.75$, $\text{pK}_{a2} = 11.65$) observed after mixing the substrate and photocatalyst was relatively low (typically 9%). At lower pH, however, this was higher reaching ca. 24% at pH 2.34. The higher adsorption of 2-HPY at lower pH may play a role for its faster photocatalytic removal at lower pH, when Cl^- anions, the scavenging capacity of which appears to increase in lower pH, are not present.

Maillard-Dupuy et al. [40] who studied the photocatalytic degradation of pyridine reported the formation of 2-HPY as a major reaction intermediate. They also suggested that hydroxyl radical attack was the most likely mechanism for 2-HPY photocatalytic destruction because the presence of a hydroxy group in the pyridine ring is likely to activate the electrophilic attack of hydroxyl radicals in ortho- and para-positions.

3.3. Combined photolytic/photocatalytic degradation of 2-FPY at 254 nm

The combined photolytic/photocatalytic degradation of 2-FPY was also studied. As discussed by Stapleton et al. [9], the photolysis of 2-FPY was faster than that of 2-CPY. Fig. 3 shows

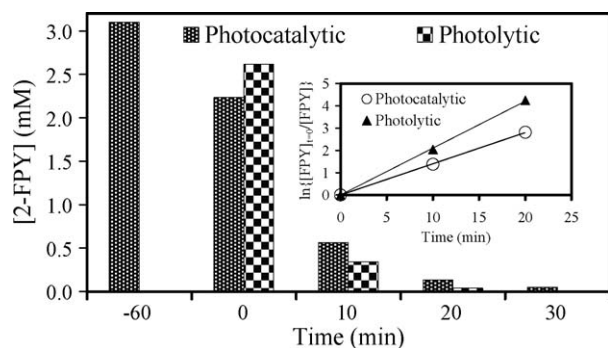


Fig. 3. Comparison of 2-FPY photolytic and photocatalytic destruction rate at 254 nm.

2-FPY concentration as a function of time for the photolytic and the combined photolytic/photocatalytic destruction at 254 nm. Similarly to its photolytic removal [9], the combined photolytic/photocatalytic removal of 2-FPY was very fast.

2-FPY photo-degradation reaction is different from that of 2-CPY because of the distinct behaviour of fluoride compared to chloride ions. Both anions are liberated very fast during the reaction. At low pH, chloride ions act as efficient hydroxyl radical scavengers. Fluoride ions, on the other hand, have the opposite effect. This may not significantly affect 2-CPY rate of removal, which was found to be practically $\cdot\text{OH}$ radical independent, but it is important for its photo-product 2-HPY further degradation. Fluoride ions displace surface bound hydroxyl groups, thus enhancing processes where hydroxyl radicals are important, as in most photocatalytic processes.

3.4. Purely photocatalytic degradation of 2-CPY and 2-FPY at $\lambda > 290$ nm: by-product elucidation and proposed reaction pathways

GC–MS analysis was performed to identify reaction by-products of purely photocatalytically treated 2-CPY and 2-FPY aqueous solutions; however, no quantitative analysis was attempted. The identified compounds produced during the photocatalytic decomposition of 2-CPY and 2-FPY, their retention times, structural formulae and similarity matches are listed in Tables 1 and 2, respectively. GC–MS analysis was also performed using 2-HPY as the substrate. No products were identified which were not found during the photocatalytic degradation of 2-CPY.

The photocatalytic product, P₁, formed from 2-CPY destruction was 2-chloro-3-pyridinol (Table 1). Unlike in the direct photolysis

of 2-CPY, a hydroxylation reaction occurs on the position 3 and the chloride position is left intact. The structure of the product suggests that hydroxyl radical attack is the mechanism by which the reaction proceeds. As mentioned earlier, however, experiments performed with $1 \text{ g L}^{-1} \text{ TiO}_2$ at 254 nm showed that 2-CPY removal rate depends on pH but it is very little affected by the presence of hydroxyl radical scavengers indicating a minor route of degradation. Similar results were observed by Sun and Pignatello [20] for the photocatalytic degradation of 2,4-D pesticide where a direct hole oxidation pathway was concluded from the fact that the reaction rate was unaffected by the addition of a hydroxyl radical scavenger.

Dines et al. [18] found that 2-CPY becomes ligated to Lewis acid sites from the nitrogen, in addition to being adsorbed by hydrogen bonding from the halogen group. More specifically, they found this behaviour for adsorption on TiO_2 , SiO_2 and ZrO_2 .

During the photocatalysis of pyridine Maillard-Dupuy et al. [40] found that the majority of the initial reaction is due to hydroxyl radical attack of the position 2 (however, adsorption in this case was due to Lewis acid ligation). In this study, it is thought that the hydroxylation of the position 3 of 2-CPY, yielding 2-chloro-3-pyridinol, occurs by adsorption of 2-CPY through the chlorine group. The presence of nitrogen in close proximity to the chloride position, stabilises in some way the C–Cl bond preventing scission. This is supported by the C–Cl bond scission found in the photocatalysis of 3-CPY [15], where the distance between chloride and nitrogen is greater.

Aramendia et al. [41] have proposed a hydroxyl radical attack for the photocatalytic degradation of 3-chloropyridine, while they suggested that the presence of chlorine atoms in alpha or beta position with respect to nitrogen in the aromatic ring will change electron density in the ring in a different manner resulting in difference in the reaction mechanism. They also proposed that 2-CPY ring may be adsorbed vertically on the catalyst surface whereas 3-chloropyridine ring did horizontally. Poulios et al. [42] reported a dual hole-radical mechanism for the degradation of the pyridine-based herbicide triclopyr in which direct hole oxidation takes place on the carboxy group, whereas hydroxyl radicals attack the pyridine nucleus.

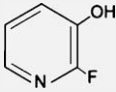
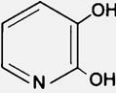
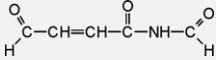
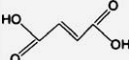

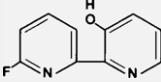
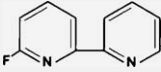
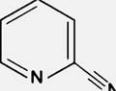
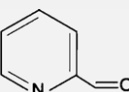
Electron transfer can occur with the substrate either gaining or losing an electron; both mechanisms have been reported extensively. Bettoni et al. [43] reported charge transfer from adsorbed lindane molecules on TiO_2 powder surfaces in an acetonitrile matrix, resulting in oxidation products. More relevant to this work is a review that was compiled on nitrogen containing

Table 1
2-CPY photocatalytic degradation products identified by GC–MS.

Compound	Name	Structure	Retention time (min)	Similarity match (%)
P ₁	2-Chloro-3-pyridinol		12.14	95
P ₂	N-Formyl-3-carbamoylpropenal		13.91	IOS ^a and Ref. [40]
P ₃	Hydroxy-acetaldehyde		6.10	72
P ₄	2-Pyridinecarboxylic acid		7.72	77

^a IOS: interpretation of spectra.

Table 2
2-FPY photocatalytic degradation products identified by GC–MS.

Product	Name	Structure	Retention time (min)	Similarity match (%)
P ₅	3-Hydroxy, 2-fluoropyridine		8.53	IOS
P ₆	2,3-Dihydroxypyridine		7.11	70
P ₂	N-Formyl-3-carbamoylpropenal		13.89	IOS and Ref. [40]
P ₇	Fumaric acid		14.20	70
P ₃	Hydroxy-acetaldehyde		6.10	79
P ₈	2,2'-5-Fluoro-4-hydroxy-bipyridine		26.54	IOS
P ₉	2,2'-5-Fluoro-bipyridine		40.51	IOS
P ₁₀	2-Pyridinecarbonitrile		20.47	78
P ₁₁	2-Pyridinecarboxaldehyde		11.97	79

aromatics [44], stating that in addition to hydroxyl radical attack, electron transfer was an important mechanism. One important difference between the work of Calza et al. [44] and the current work is that none of the reported in Ref. [44] substrates involved halogen groups. Subsequently, ligation to catalyst sites by the halogen atom was not contributing. Additionally, 2,4,6-trichlorophenol was treated in the presence of Degussa P-25 by Hurum et al. [45]. They postulate that two mechanisms of electron transfer to the catalyst exist through ligation of chloride or OH positions, depending on the mode of adsorption. On the other hand, Dimitrijevic et al. [46] found that in the case of pyrroloquinoline quinone, electron transfer occurs from the conduction band electrons of TiO₂ to the adsorbed substrate. This phenomenon was also observed in the photocatalysis of nitrobenzene using Degussa P-25 [47]. The authors used de-oxygenated aqueous solutions to remove competition between the substrate and O₂ for TiO₂ conduction band electrons. 2-Propanol was also used to scavenge valence band holes, thus eliminating the hydroxyl radical reaction pathway. Panayotov and Yates [48] compared aromatic organic substrates containing Cl and/or S atoms. They found that Cl acts as an electron acceptor for the trapped electrons of TiO₂ while this was not found for the S atom.

As mentioned before, the observation of the present study that 2-CPY removal rate is very little affected by the presence of hydroxyl radical scavengers indicates that hydroxyl radical attack

may be a minor route for chemical reaction. The major route could be attributed to that reported previously [49,50] for benzo[b]pyridine (quinoline) and 2-chloroquinoline molecules containing a pyridine and 2-chloro-pyridine moieties respectively, that react predominantly via formation of a radical cation by electron transfer to the TiO₂ valence band (i.e. hole capture). The reaction mechanism proceeds via addition of superoxide (O₂^{•−}) or O₂ to the quinoline radical cation leading to subsequent ring opening.

N-formyl-3-carbamoylpropenal, product, P₂, was also identified in the degradation of pyridine [40]. The mass spectrum of P₂ is similar to that reported in Ref. [40], together with the analysis of the different ion fragments, while the molecular ion at *m/z* = 127 is also present. The degradation of the latter aliphatic product could then result in the production of short-chain compounds such as maleamic acid, butenedial [40], formamide [40,44,51], hydroxy acetaldehyde (compound P₃) and short-chain carboxylic acids like acetic and formic [40,52,53]. The formation of 2-pyridinecarboxylic acid, compound P₄, can be explained by the reaction of the substrate, 2-CPY, with formic acid, which is formed in the later stages of the degradation process. Mass spectra of compound P₄ present a loss of CO₂ (M⁺−44) and the fragmentation of 2-chloropyridine. Reaction of later stage products with substrate is common place in photocatalysis [40,53].

There were found to be two processes involved in the initial degradation of 2-FPY. Unlike 2-CPY, C-halogen bond scission was

found to occur in conjunction with hydroxylation of the position 3. The latter of these reactions forms 3-hydroxy-2-fluoropyridine, product P_5 , which was not listed in the GC–MS library. Its identification was based on the interpretation of its mass fragmentation pattern shown as [Supplementary Material \(Figure A\)](#).

The molar mass of 3-hydroxy-2-fluoropyridine is 113 that corresponds to a main mass peak. The base peak at m/z 85 could correspond to the loss of either NCH_2 or CO groups. Also the peaks at m/z 58 and 93 correspond to the loss of $CHO-CH=CH^+$ and HF, respectively. Finally, the peak at m/z 39 corresponds to the group $C_3H_3^+$ and is also reported in the mass spectra of hydroxypyridine [40]. The proposed pathway of its formation is electrophilic OH addition at position 3.

The formation of product P_6 requires the removal of fluorine and the subsequent hydroxylation of the fluorine position to yield 2,3-dihydroxypyridine that is in equilibrium with its tautomeric form 3-hydroxy-2(1H)-pyridinone. Although C–F bond energy is larger than that of C–Cl bond energy, it is the combination of bond energy, electronegativity and atom size that contribute to the dissociation of fluoride from 2-FPY. More specifically, the ability of the halogen to retain the TiO_2 donated electron is very important. Fluorine is the most electronegative of all halogens, predominantly due to its lowest atom size. Hence, it has an increased ability to retain an extra outer shell electron. It is, thus, possible that the donated by TiO_2 electron is retained by fluorine, as opposed to migration to the aromatic ring, which is more likely with other halogens. Thus, it is plausible that a portion of the photocatalysed 2-FPY is subjected to C–F bond scission through fluorine electron retention. In a photocatalytic study of all 4-halogenated phenols O'Shea and Cardona [54] found that the reaction rate of photocatalysis of 4-fluorophenol was the highest. The authors found that the order of reaction rates of the different 4-halogenated phenols was inverse to the bond strength of the C-halogen bond. They supported a mechanism involving an addition of hydroxyl radical followed by elimination of halide. They suggested the formation of a radical intermediate complex of the substrate adsorbed on TiO_2 . In another work, Minero and Aliberti [55] studied the photocatalytic degradation of various fluorinated phenols. The authors identified a range of hydroxylated products, both fluorinated and non-fluorinated in nature. They found that both 2- and 4-fluorophenol are subjected to hydroxylation on the fluorine position via hydroxyl radical attack. Thus, another possible mechanism could be the addition of OH to the C atom carrying the F atom, followed by a rapid elimination of HF [56]. Both mechanisms are consistent with the suggestion made in the present study, i.e. that parallel hydroxylation and defluorination may occur. Following the hydroxylation of the position bearing the F atom, ring opening occurs and degradation products such as P_2 , N-formyl-3-carbamoylpropenal, and P_3 , hydroxyacetaldehyde, were formed as in the case of 2-CPY photocatalytic degradation.

Compound P_7 , fumaric acid, was identified with a lower similarity match of 70%. The GC–MS chromatogram peak was also small in comparison to other compounds. Low et al. [51] and Leyva et al. [52] suggested that fumaric acid was a degradation product in the photocatalysis of pyridine. A series of hydroxyl radical reactions lead to the formation of final stage organic products, such as carboxylic acids (formic and acetic acids) and finally to carbon dioxide and water. The fate of nitrogen is presumed to be ammonia and nitrate as reported in Ref. [40] dealing with the photocatalysis of pyridine.

In parallel with the formation of P_6 , the radical formed following the aforementioned C–F bond scission participates in two further reactions. The first of those is a dimerisation reaction forming the dimmers P_8 and P_9 . Scission of the C–F bond in the 3-hydroxy-2-fluoropyridine (P_5) produces 3-hydroxypyridine radi-

cal (P_5^*) which reacts further with a substrate molecule to form compound P_8 . Compound P_8 identification was based on interpretation of the mass fragmentation pattern shown in [Supplementary Material \(Figure B\)](#).

The molar mass of compound P_8 matches the main mass peak at m/z 190. The peak at m/z 189 corresponds to the loss of one hydrogen atom. The peaks at m/z 162 and 135 correspond to the loss of CO^+ and $HOC-CH=CH^+$, respectively. The peak at m/z 172 most likely corresponds to the loss of H_2O (M^+-18) a typical loss for hydroxy-compounds. The peak at m/z 96 corresponds to fluoropyridine ring produced by the fragmentation of the dimer P_8 . Finally the peaks at m/z 78 and 39 correspond to the pyridine ring and $C_3H_3^+$ group, respectively. The retention time of compound P_8 , 26.54 min, is consistent with the high retention times of other dimmers identified in this study.

Scission of the C–F bond in the 2-FPY producing a pyridine radical which reacts further with a substrate molecule to form compound P_9 . Compound P_9 was not listed in the GC–MS library; its identification was based on the interpretation of mass spectrum shown in [Supplementary Material \(Figure C\)](#), as follows: The molar mass of the compound corresponds to the main mass peak at m/z 174. The peak at m/z 173 corresponds to the loss of hydrogen, while the peak at m/z 147 could be the result of $C_2H_2^+$ and $C_2H_3^+$ loss. Also, the peaks at m/z 78 and 96 sum up to m/z 174, with m/z 78 and 96 corresponding to the pyridine and fluoropyridine ring fragments. Maillard-Dupuy et al. [40] proposed that the dipyrindine dimer formed through the photocatalysis of pyridine was a reaction initiated through the formation of a pyridine radical. The molecular ion peaks were also monitored as the base peaks for 2,2' and 2,4' dipyrindyls.

Finally, the detection of coupling products confirmed that 2-FPY photocatalytic destruction follows a radical mechanism. Detection of coupling reactions in photocatalytic degradation of halogenoaromatics and N-heterocyclic aromatics has already been reported in the literature [40,29,49,53].

The second possible pathway is the reaction of pyridine radical produced from the C–F bond scission of the substrate with later stage degradation products such as formamide and acetic acid to form compounds 2-pyridinecarbonitrile (P_{10}) and 2-acetylpyridine (P_{11}), respectively. P_{10} could be rationalized through the formation of 2-carbamoylpyridine, as a result of reaction of formamide and pyridine, that could be dehydrated during the GC–MS analysis. The mass spectra of P_{10} matched also that reported in Ref. [40]. Similarly to our study, 2-carbamoyl pyridine was detected elsewhere [40] at high initial concentration of pyridine.

3.5. Combined photolytic/photocatalytic TOC reduction of 2-CPY, 2-FPY and 2-HPY

Mineralisation of 2-CPY upon irradiation at 254 nm was studied employing varying concentrations of Degussa P-25 TiO_2 photocatalyst. The TOC and pH history of these experiments, for catalyst concentrations in the range of 0–1 g L⁻¹, can be seen in [Fig. 4](#). Open markers have been used to indicate normalised TOC values. For each measurement the respective pH variation with time is shown with a continuous line where a few closed markers of the same shape as the respective TOC curve have been added to serve as pH-curve identifiers. In other words, the measurement of the pH was continuous; the markers have been only used for the better visualisation of the figure. (This is also the case for [Figs. 6 and 7](#).) As can be seen in [Fig. 4](#), photocatalyst concentration had no significant effect on the overall TOC removal time. On the other hand, for experiments performed with the use of an overhead condenser operating at -10°C , TOC removal was slower, accompanied by a slower rise in the pH, thus indicating that acidic volatile compounds are escaping from the system.

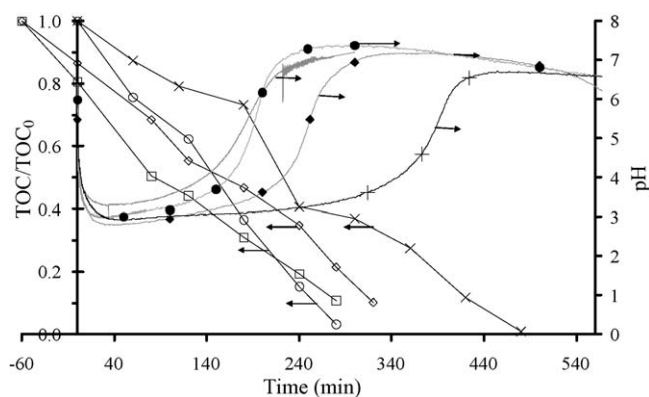


Fig. 4. Normalised TOC and pH history of combined photolytic/photocatalytic 2-CPY mineralisation at different photocatalyst loadings in the range of 0–1 g L⁻¹. (□) TOC, 1 g L⁻¹ of photocatalyst and (—) pH of the same measurement; (◇) TOC, 0.05 g L⁻¹ of photocatalyst and (◆) pH of the same measurement; (○) TOC, 0 g L⁻¹ of photocatalyst and (●) pH of the same measurement; (X) TOC, 0 g L⁻¹ of photocatalyst, use of overhead condenser and (+) pH of the same measurement.

The first stages of the combined photolytic/photocatalytic 2-CPY destruction are shown in Fig. 5, where all products but the two di-hydroxypyridines identified in Ref. [40] as 2-HPY by-products, have been identified analytically in our work.

Often direct photolysis is more effective than photocatalysis in reducing the larger early degradation products to smaller, more volatile products. On the other hand, photocatalysis is more effective at removing smaller, volatile aliphatic compounds [57,58]. However, with aeration these smaller products may partially be stripped from solution. This was verified repeating the experiment with the use of a condenser, where, in an otherwise identical system, the TOC removal rate was reduced, as can be seen in Fig. 4. Therefore, only relative comparisons on the mineralisation effectiveness of the applied treatment can be made. Larger scale wastewater treatment processes based on TiO₂ photocatalysis need to operate under air purging. Dissolved oxygen is required in the photocatalytic system

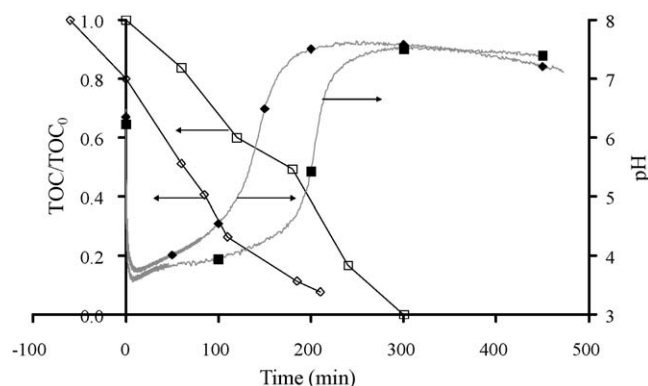


Fig. 6. Normalised TOC and pH history of 2-FPY mineralisation with and without photocatalyst. (□) TOC, no photocatalyst and (■) pH of the same measurement; (◇) TOC, 1 g L⁻¹ TiO₂ and (◆) pH of the same measurement.

as organic pollutants react with hydroxyl radicals to form organic radicals, which then rapidly react with dissolved oxygen to form various degradation products [50,53,59]. Moreover, dissolved oxygen is adsorbed onto the catalyst surface, forming the superoxide radical via electron transfer. This reduces the electron–hole recombination rate within the catalyst and produces a secondary radical for the degradation of the organic material [50]. On the other hand, the main 2-CPY photolytic product, i.e. 2-HPY, which is formed even in the presence of 1 g L⁻¹ of catalyst, is fast destroyed via photooxidation [10], thus, the supply of air in the system is necessary for its destruction. Experiments performed in the dark under vigorous purging with air (400 mL min⁻¹) showed that neither 2-CPY nor 2-HPY was stripped off the solution at the conditions of the measurement. Moreover, measurements taken over a period of a few weeks showed that neither 2-CPY nor 2-HPY concentration dropped when stored in a closed system in the dark.

The combined photolytic/photocatalytic (Fig. 6) degradation of 2-FPY shows a reduced TOC removal time compared to that of photolysis alone. 90% of TOC disappearance was observed in ca.

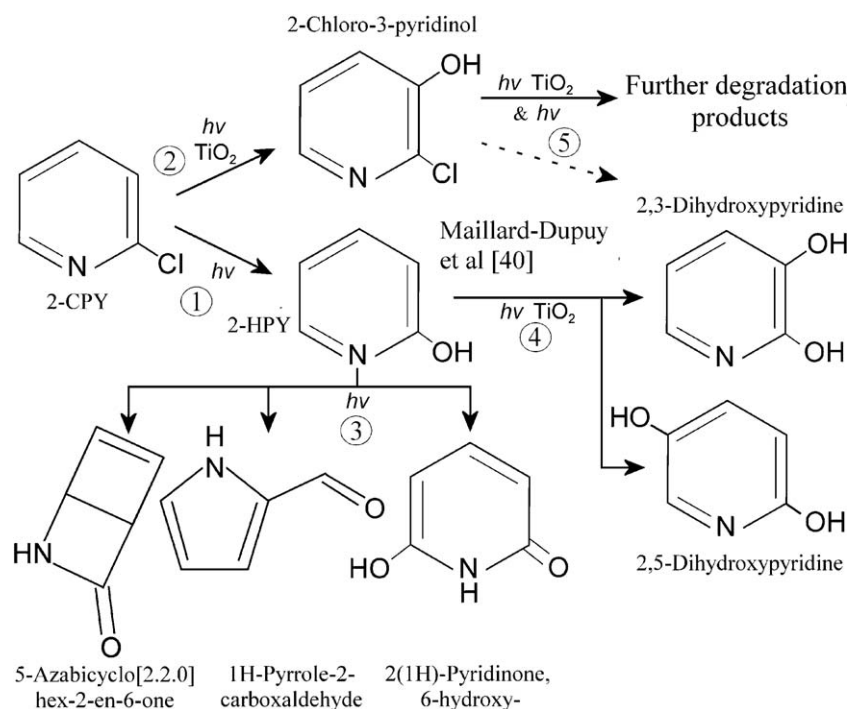


Fig. 5. Key early stage intermediate compounds and reaction pathways during the 2-CPY combined photolytic/photocatalytic degradation. Formation of 2,3-dihydroxypyridine and 2,5-dihydroxypyridine has also been proposed by Maillard-Dupuy et al. [40].

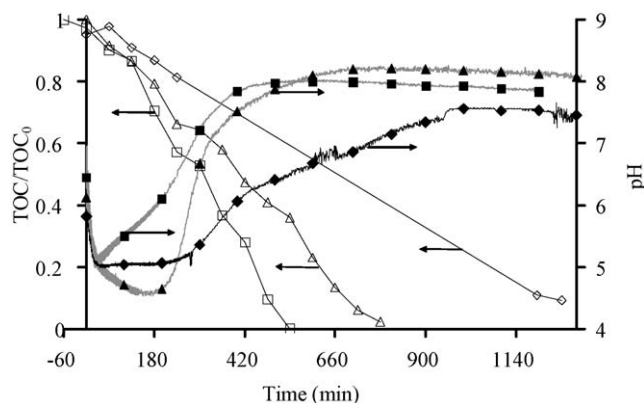


Fig. 7. Normalised TOC and pH history of 2-HPY mineralisation with and without photocatalyst with and without air purging. (□) TOC, air purging and $1 \text{ g L}^{-1} \text{ TiO}_2$ and (■) pH of the same measurement; (◇) TOC, no air purging and $1 \text{ g L}^{-1} \text{ TiO}_2$ and (▲) pH of the same measurement; (△) TOC, air purging, no photocatalyst and (▲) pH of the same measurement.

200 min with 1 g L^{-1} photocatalyst addition as opposed to ca. 280 min without photocatalyst. Much of this reduction can be associated with adsorption of the organic material onto the photocatalyst. However, it is apparent that the addition of photocatalyst enhances 2-FPY degradation much more than that of 2-CPY because of the presence of fluoride ions as mentioned earlier.

The TOC removal during degradation of 2-HPY under different conditions is shown in Fig. 7. The presence of photocatalyst accelerates substantially its mineralisation compared to the other two non-catalytic experiments. Purging with air reduces the mineralisation time; this is attributed not only to the enhanced photooxidation of 2-HPY, but also to the aforementioned stripping effects. Nevertheless, for stripping effects to have a measurable effect, the concentration of the smaller volatile compounds in the solutions needs to be substantial. The degradation process however, has to proceed appreciably before they are formed in such concentrations. In all cases, the degradation of 2-HPY was found to be slower than that of the same initial quantity of 2-CPY.

The electron transfer reactions of 2-CPY (and to a lesser extent of 2-FPY) are believed to be dominant due to surface adsorption from the halogen group. The photocatalytic degradation of 2-HPY is believed to predominantly proceed via hydroxyl radical attack. Thus, as the substrates become dehalogenated, the role of hydroxyl radicals is believed to increase because addition of OH group activates the ring towards electrophilic substitution.

4. Conclusions

The combined photolytic/photocatalytic (TiO_2) degradation and mineralisation of 2-CPY, 2-FPY and 2-HPY was studied by means of ultraviolet irradiation at 254 nm in a range of conditions. Their photocatalytic degradation at wavelengths above 290 nm was also investigated to identify the key intermediate compounds formed.

pH had a substantial impact on 2-CPY photocatalytic removal rate. It was faster at near neutral pH. 2-CPY removal rate at solution natural pH and at near neutral pH was practically unaffected by the presence of radical scavenger.

2-HPY photocatalytic removal is faster at lower pH but the presence of chloride anions, which act as radical scavengers, had a detrimental effect on its removal rate. Their scavenging effect was more significant at low pH. On the other hand, F^- and SO_4^{2-} anions accelerated its removal.

Decomposition products were identified and their formation is justified. 2-hydroxypyridine and 2-chloro-3-pyridinol are the first major intermediates produced by 2-CPY, photolysis and photocatalysis, respectively. Hydroxyacetaldehyde, 2-pyridinecarboxylic acid and N-formyl-3-carbamoylpropenal were identified as later products formed from purely photocatalytic destruction of 2-CPY. The products identified from purely photocatalytic destruction of 2-FPY were rationalized through hydroxylation, defluorination, ring-opening and coupling reactions.

Complete TOC removal was achieved in all cases. Photocatalytic TOC removal was faster than the photolytic one under the same otherwise conditions, for all three compounds studied here.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2009.12.015.

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